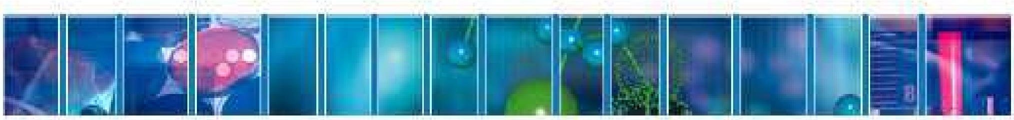


E-MRS

2012 Spring Meeting

May 14 – 18
Strasbourg, France

PROGRAMME

CONFERENCE SYMPOSIA

MATERIALS FOR ENERGY

A Advanced Silicon Materials Research for Electronic and Photovoltaic Applications III
B Thin Film Chalcogenide Photovoltaic Materials
C Solid State Ionics: Mass and Charge Transport across and along Interfaces of Functional Materials
D Unconventional Thermoelectrics: from new materials to energy conversion devices
E Actinide compounds and properties
F Solid proton conductors (In honor of Prof. G. Alberti)

BIO / ORGANIC / POLYMERIC MATERIALS

G Functional Biomaterials
H Organic and Hybrid Materials for Flexible Electronics: Properties and Applications
I Biological applications for organic electronic devices
J DNA Directed Programmable Self-assembly of Nanoparticles into Meta Materials for energy and other applications
K Surface modifications of carbon-related materials II

MATERIALS FOR ELECTRONIC / PHOTONIC / PLASMONIC

L Novel Functional Materials and Nanostructures for innovative non-volatile memory devices
M More than Moore: Novel materials approaches for functionalized Silicon based Microelectronics
N Control of light at the nanoscale: materials, techniques and applications
O Applied Nanoplasmonics: Nanoplasmonic Functional Materials and Devices

ADVANCED MATERIALS AND NANO MATERIALS

P Advanced Hybrid Materials II: design and applications
Q Novel materials and fabrication methods for new emerging devices
R Science and technology of nanotubes, graphene and 2D layered materials
S Novel materials for hetereogeneous catalysis
T Physics and Applications of Novel gain materials based on Nitrogen and Bismuth Containing III-V Compounds
U Carbon- or Nitrogen-Containing Nanostructured Thin Films

METHODS AND ANALYSIS

V Laser materials processing for micro and nano applications
W Current Trends in Optical and X-Ray Metrology of Advanced Materials for Nanoscale Devices III
X Quantitative Microscopy of Energy Materials
Y Advanced materials and characterization techniques for solar cells

procedures and multi-parametric analyses to better characterized the inhomogeneous material obtained. Herein, we propose the implementation of novel chemical apparatuses as a controlled, efficient and sustainable approach for the scalable chemical functionalization of CNTs.1 In particular, we have investigated the functionalization of CNTs with classical reactives, including azomethinylides, diazonium salts and organolithium compounds, in flow conditions. The characterization of these products with a set of subsidiary techniques (UV-vis and Raman spectroscopy, TGA, DLS) shows that our approach affords products tailorable for specific applications, with a particular interest for the controlled compatibilization in polymeric organic solar cells.2 1. (a) Salice, P.; Menna, E., et al., Chem. Commun. 2011, 47 (32), 9092-9094; (b) Menna, E.; Salice, P., et al. Italian Patent PD2011A000153. 2. Cataldo, S.; Salice, P., Menna, E.; Pignataro, B., Energy Environ. Sci. 2012, doi: 10.1039/C1EE02276H.

add to my program (close full abstract)

11:15 **The effect of carbon nanotube tip functionalization on electronic tunneling.**

Authors : Sergey V. Pyrlin [1,2]; Marta M.D. Ramos [1]; Peter D. Haynes [3]; Nicholas Hine [3].

Affiliations : 1. Group of Computational and Theoretical Physics, Center of Physics and Department of Physics, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal; 2. I3N - Institute for Nanostructures, Nanomodelling and Nanofabrication, IPC - Institute for Polymers and Composites, University of Minho, Campus de Azurem, 4800-058 Guimaraes, Portugal; 3. London Center for Nanotechnology, Department of Materials, Imperial College London, Exhibition Road, SW7 2AZ London, United Kingdom;

Resume : Modification of carbon nanotubes by doping and functionalization is widely used to control individual nanotubes' properties and interaction with surrounding media such as polymer matrix. As it is known from experiments and theoretical calculations, sidewall modification can increase nanotube-matrix interaction but reduce nanotube conductivity significantly. In this work we investigate the effect of doping and functionalization on carbon nanotube tip electrical properties. Using density functional calculations, we show that doping with boron and nitrogen and functionalization with –COOH group modify the local density of electronic states of several nanotube tip models, which can boost or decrease tunneling currents between carbon nanotubes while having negligible effect on individual nanotube conductivity itself. Thus, a possibility is opened to increase electrical characteristics of CNT based materials and devices by tip region modification and selecting appropriate type and amount of dopant/chemical group. This work is a part of Marie Curie Initial Training Network "CONTACT" (FP7-PEOPLE-ITN-2008-238363) http://www.contactproject.eu/.

R10 10

add to my program (close full abstract)

11:30 **3-D Nanostructured Si-Ge-Single Wall Carbon Nanotube Free-Standing Anodes for High Energy Density Lithium Ion Batteries**

Authors : Roberta A. DiLeo, Melissa Thone, Michael W. Forney, Matthew J. Ganter, Jason Staub, Reginald E. Rogers, Brian J. Landi

Affiliations : Nanopower Research Laboratories, Microsystems Engineering Program, Golisano Institute for Sustainability, Department of Chemical and Biomedical Engineering

Resume : Alternative active materials for lithium ion batteries are under investigation to meet energy storage demands. Silicon and Ge are promising anode materials demonstrating capacities up to 3000 mAh/g, much higher than state-of-the-art graphite. Recent work shows free-standing single wall carbon nanotubes (SWCNTs) as viable anode support materials due to their robust mechanical and electrical properties. A 3-D hybrid structure of Ge and SWCNTs which enhances lithium diffusion has demonstrated 1000 mAh/g capacity at a C/20 rate with < 8 % reduction in energy density as the discharge rate is increased to 1C in full batteries. The electrochemical performance of nanostructured electrodes containing both Si and Ge within a SWCNT network is presently evaluated. Ge nanoparticles are incorporated into SWCNT electrodes by solution processing, and Si is deposited through a chemical vapor deposition process. Characterization of the materials by Raman spectroscopy, XRD, and SEM confirm the presence of Ge within the CNT network coated with a thin layer of Si. Electrochemical testing of the Si-Ge:SWCNT electrodes shows high reversible capacity exceeding 1000 mAh/g. The addition of the Si coating enhances the electrode capacity along with reducing the surface area and the first cycle loss, resulting in a high

R10 11

The effect of carbon nanotube tip functionalization on electronic tunneling

Sergey V. Pyrlin* [1,2,3]; Marta M.D. Ramos [1]; Peter D. Haynes [4]; Nicholas Hine [4]

1. *Group of Computational and Theoretical Physics, University of Minho, Portugal;* www.gfct.fisica.uminho.pt
2. *I3N - Institute for Nanostructures, Nanomodelling and Nanofabrication, Portugal;* www.i3n.org
3. *Bauman State Technical University, Russia;* www.bmstu.ru
4. *Imperial College London, United Kingdom;* http://www3.imperial.ac.uk/

**pyrlinsv@fisica.uminho.pt*

This project has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement no. 238363

CONTACT

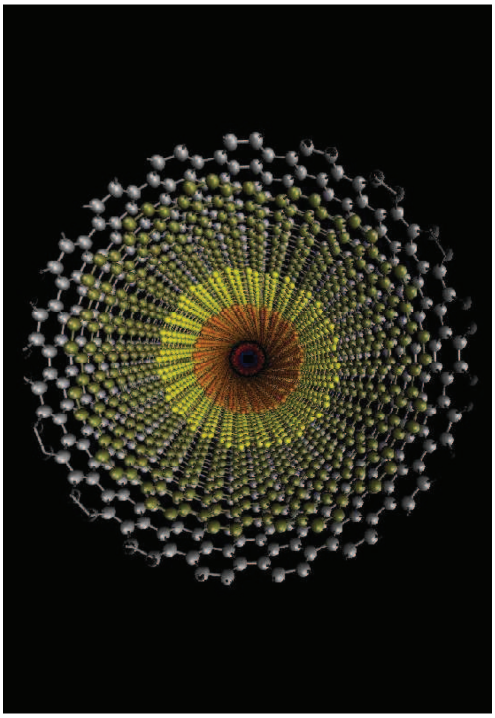
ITN "CONTACT": http://www.contactproject.eu/

The research aim of ITN "CONTACT" is the tailored industrial supply-chain development of CNT-filled polymer composites with improved mechanical and electrical properties

Synthesis	Modeling	Processing
Dispersion	Characterization	Application

This project has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement no. 238363

Applications of polymer-CNT composites:



* Photographs from www.baytubes.com

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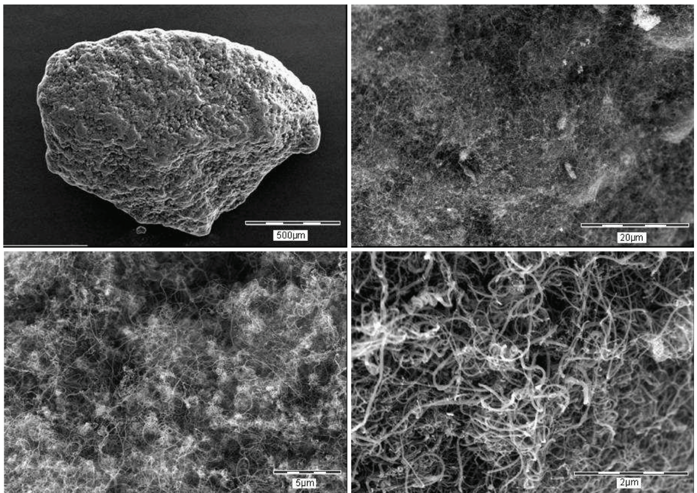
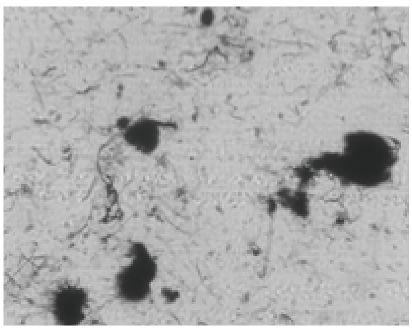
Industrial scale CNT production:

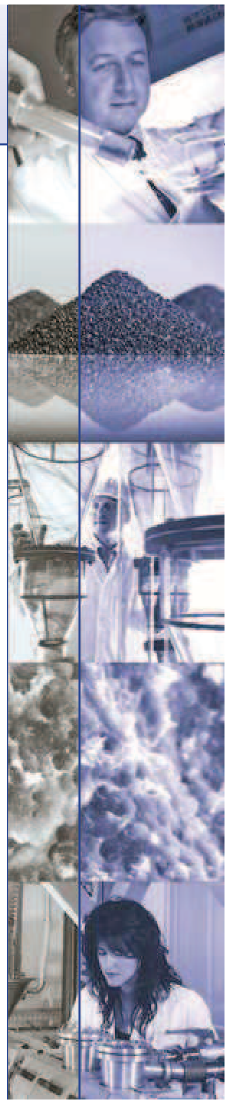


* Micro photograph from www.baytubes.com

- I've made a composite with 2 w.% of nanotubes!

- Indeed… and looks like all of them are here.





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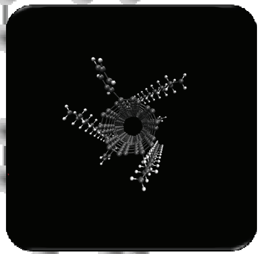
Project overview:

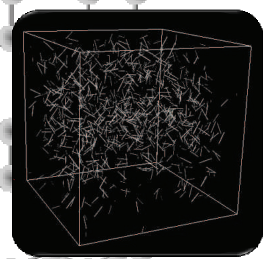
Atomistic level

- **Input:** atomic data, molecular geometry
- **Methods:** QC & MD
- **Results:** (modified)CNT properties – IP,EA, charge hopping probabilities etc.;



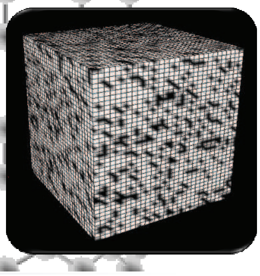
Mesoscopic level

- **Input:** composite morphology, external fields, molecular properties;
- **Methods:** MC;
- **Results:** composite FE properties;



Application: Continuum level

- **Input:** device design, material properties;
- **Methods:** FEM, analytical modeling etc.;
- **Results:** device properties;



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This project has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement no. 238363

Imperial College London

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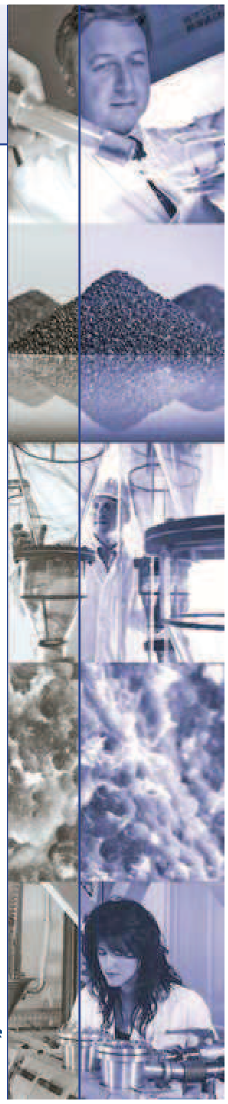
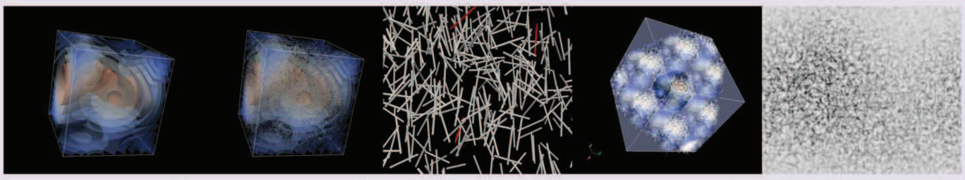


P1.11: GPGPU-assisted nanocomposite modeling and characterization

Sequence of generation of microphoto-scale computational models for analysis and simulation.



Predefined distribution density → "CNT web" following the distribution → Intersection correction → Periodic conditions → "Real-like" system for simulation & analysis

Rates of filling 168 um cube with 4um x 10 nm cylindrical inclusions:

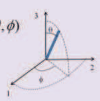
NVIDIA GTX 480	0.5 vol % uniform distribution	$18*10^6$ inclusions	5.0 min	NVIDIA Tesla C2050	1.0 vol % uniform distribution	$36*10^6$ inclusions	33.5 min
NVIDIA GTX 480	0.5 vol % nonuniform distribution	$18*10^6$ inclusions	9.2 min	NVIDIA Tesla C2050	1.0 vol % nonuniform distribution	$36*10^6$ inclusions	155 min

Examples of applications:

Estimation of composite mechanical properties depending on CNF orientation:

$$C=(V_m C_m + V_f \langle C_f A^{MT}\rangle)(V_m I + V_f \langle A^{MT}\rangle)^{-1}$$

$\rho(\theta,\phi)$



$$\langle A^{MT}(\theta,\phi)\rangle = \frac{\int_0^{2\pi}\int_0^{\pi} \bar{A}^{MT}(\theta,\phi)\rho(\theta,\phi)\sin(\theta)d\theta d\phi}{\int_0^{2\pi}\int_0^{\pi}\rho(\theta,\phi)\sin\theta \mathrm{d}\theta\mathrm{d}\phi}$$

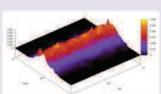
(Mori-Tanaka theorem of averages stresses in matrix)

$$A^{MT} = A^{Eshelby}((1-V_f)I + V_f A^{Eshelby})^{-1}$$

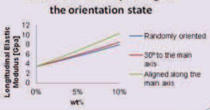
(Eshelby Equivalent inclusion method)

$$A^{Eshelby} = (I + ES_m(C_s - C_m))^{-1}$$

Simulated orientation distribution:

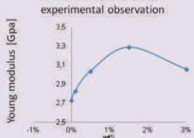


Elastic modulus depending on the orientation state

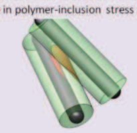


Inclusions' contact surface area evaluation and properties correction:

Tensile tests (CNF/Epoxy) – experimental observation

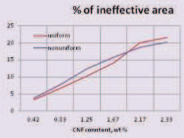


The fiber surface area between 2 fibers doesn't participate in polymer-inclusion stress transfer



With the increase of nanofiber content the ineffective surface area increases up to 20 % by 2 wt%.
Change in total ineffective area depending on nanofiber distribution can be observed directly.

% of ineffective area



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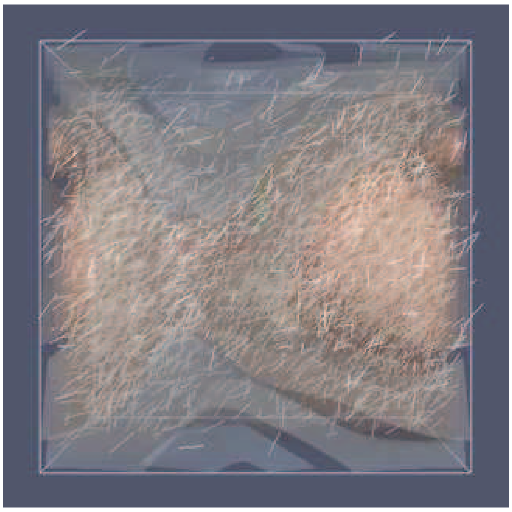
Mesoscopic level modeling:



Current inside CNT ~mA;
Current in tunneling junctions ~ nA;
Ratio of effective time of *inter*- & *intra*tube transport:

$$t_{tun}/t_{CNT} \sim 10^5$$

Mesoscopic Simulation:
Monte Carlo simulation of charge transport between CNTs under effect of:

$$\vec{E}_{loc}(\vec{r}) = \vec{E}_{ext}(\vec{r}) + \vec{E}_{e}(\vec{r}) + \vec{E}_{T}(\vec{r}) + \vec{E}_{pol}(\vec{r})$$

Field of free charges: $\vec{E}_e(\vec{r}) = \sum \frac{e}{r_{ij}}$

Polarization field: $\vec{E}_{pol}(\vec{r}) = \sum \vec{E}_i^{dipole} = \sum \frac{3(\vec{p}_{T,pol}\vec{r}_{ij}) - r_{ij}^2 \vec{p}_{T,pol}}{r_{ij}^5}$ $\quad \vec{p}_{pol} = \alpha_{ij}\vec{E}$

Thermal voltage fluctuations in contact region $f(V_T) = A_T exp\left(-\frac{CV^2}{2k_BT}\right)$

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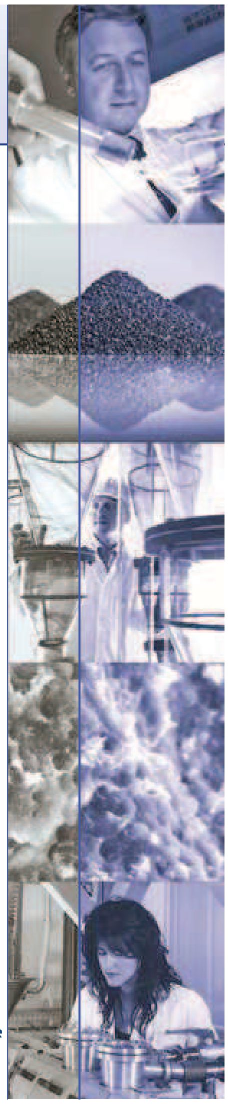
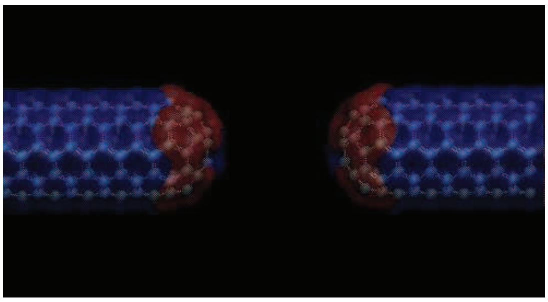
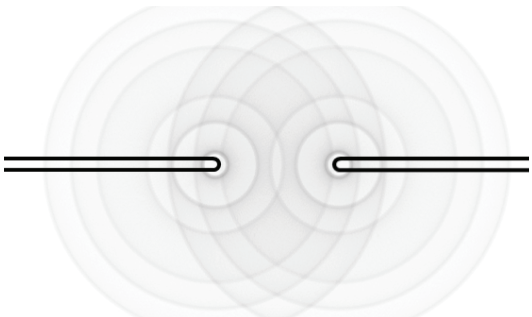
Electron transfer in the "tip region":







$$W_{tot} = \frac{4\pi}{\hbar}\int_0^{eV} \rho_s(E_F - eV + \varepsilon)\rho_D(E_F + \varepsilon)|M|^2 d\varepsilon \qquad M_{\varphi\psi} = \frac{\hbar}{2m}\int (\varphi^*\nabla\psi - \psi\nabla\varphi^*)dS$$

Tersoff – Hamann:*

$$\psi_n = \frac{A_n \exp(-k_n r)}{r} \qquad k_n = \frac{\sqrt{2m|E_n|}}{\hbar} \qquad \Rightarrow \qquad M_{ij} = \frac{\hbar}{2m}\frac{k_i k_j}{2\pi h} e^{-(k_i+k_j)h}$$

Data required from atomistic level: LDOS ρ(E) in contact region

* *Theory of the scanning tunneling microscope*
J. Tersoff, D.R. Hamann, PRB 1985 Vol. 31(2) 805-813;

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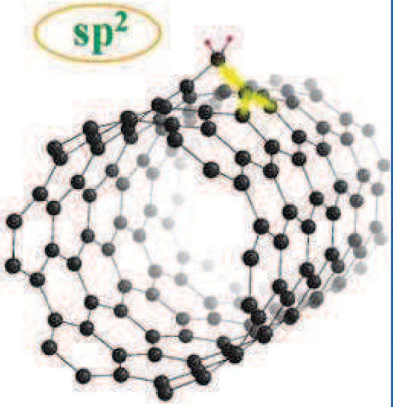
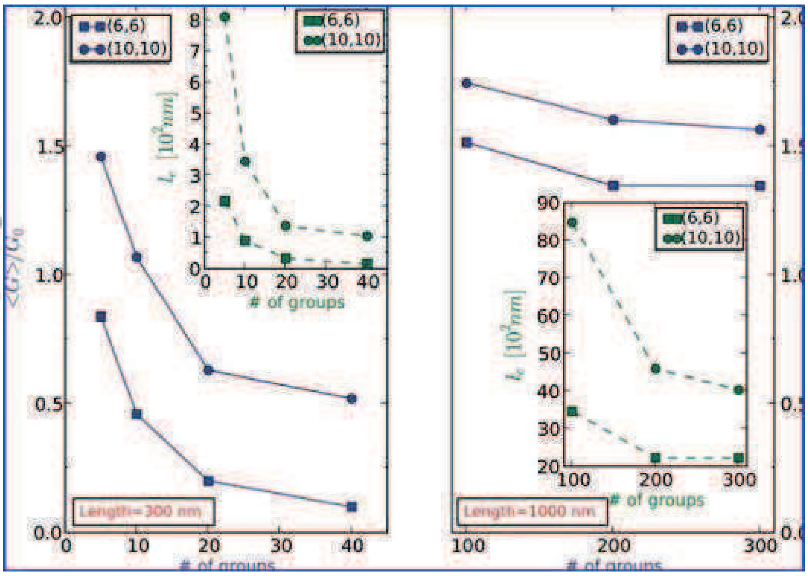
Intratube transport: decrease of conductivity with doping

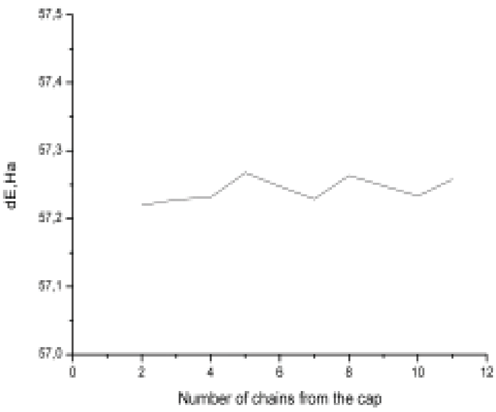


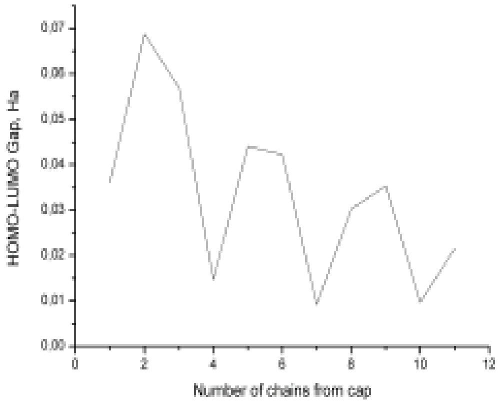


Effect of the Chemical Functionalization on Charge Transport in Carbon Nanotubes at the Mesoscopic Scale
Alejandro Lo´ pez-Bezanilla, Nano Letters 2009 Vol. 9 (3) 940-944;

This project has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement no. 238363

Properties variation in finite tube fragments:





Variation of electronic density:

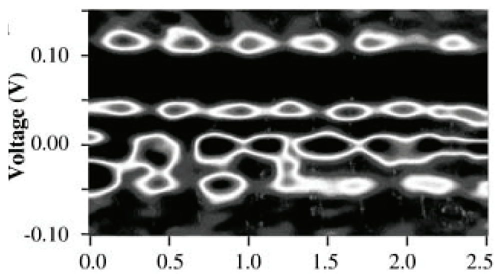
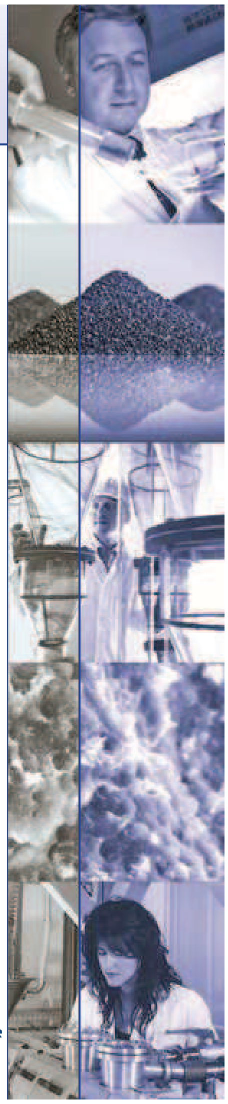


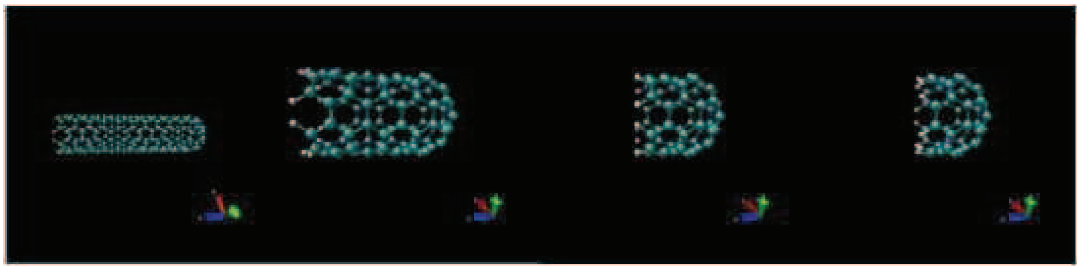
Image compiled from ~100 dI/dV measurements
Odom T.W., Hafner J.W., Lieber C.M. Scanning probe microscopy studies of carbon nanotubes
M. S. Dresselhaus, G. Dresselhaus, Ph. Avouris (Eds.): Carbon Nanotubes,
Topics Appl. Phys. 80, 173–211 (2001)

This project has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement no. 238363

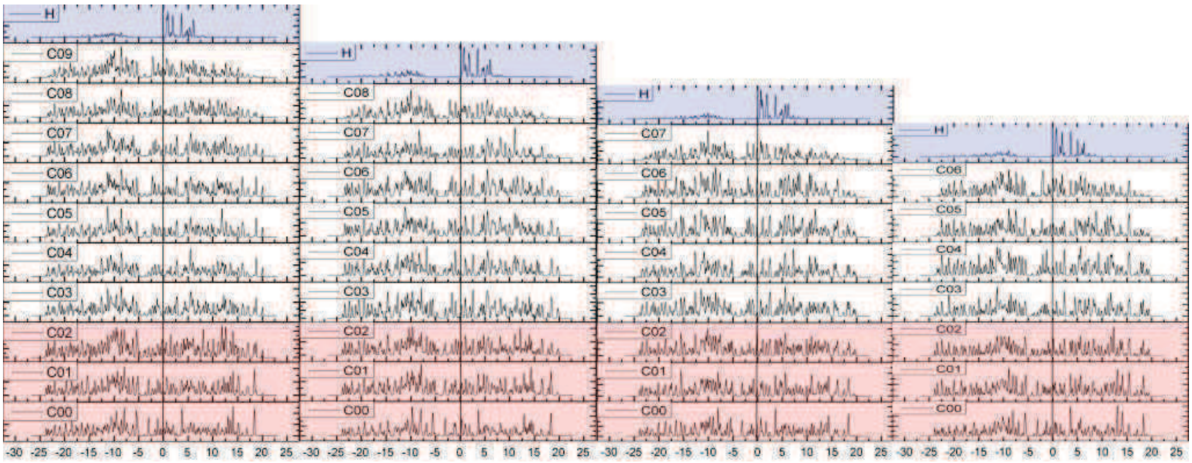


CONTACT

CNT-tip models:



CNT-tip LDOS for the tubes with 4-7 layers:



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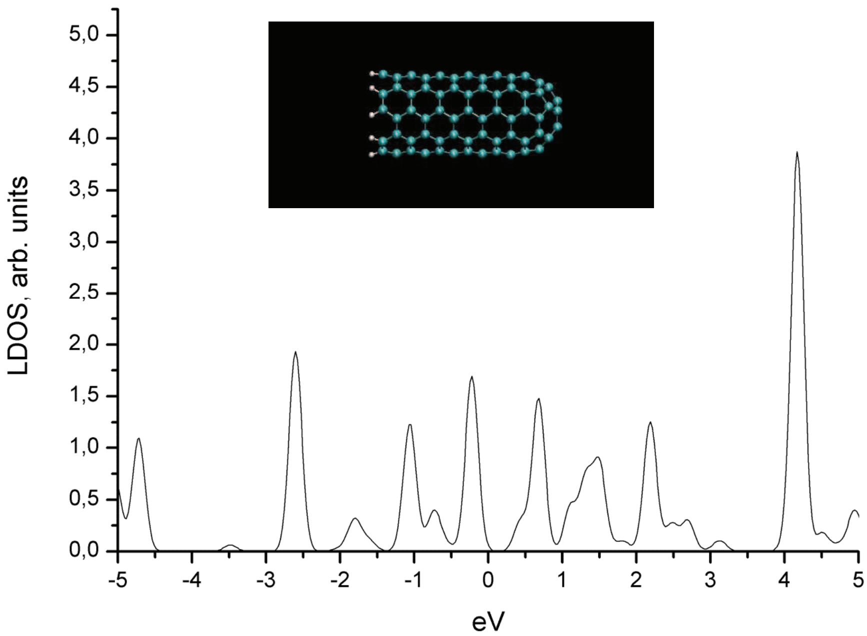
LDOS for the pure CNT tip :



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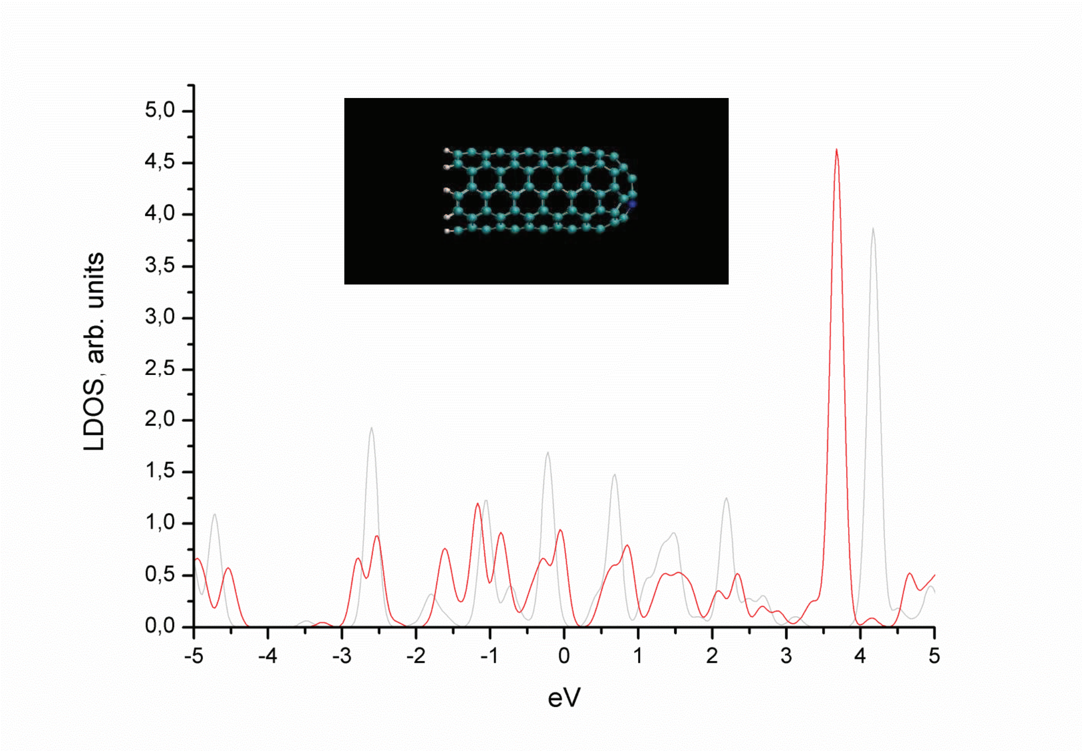
LDOS for the CNT tip with N adatom: *peak displacement, additional peaks; gap narrowing*



This project has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement no. 238363

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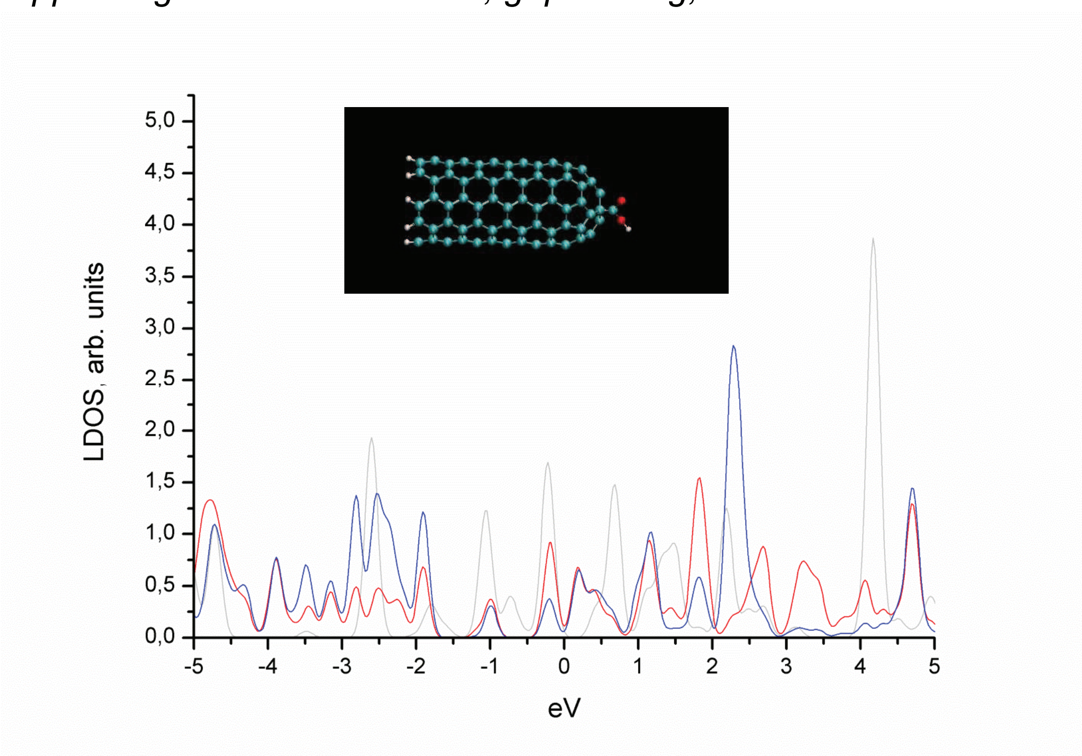
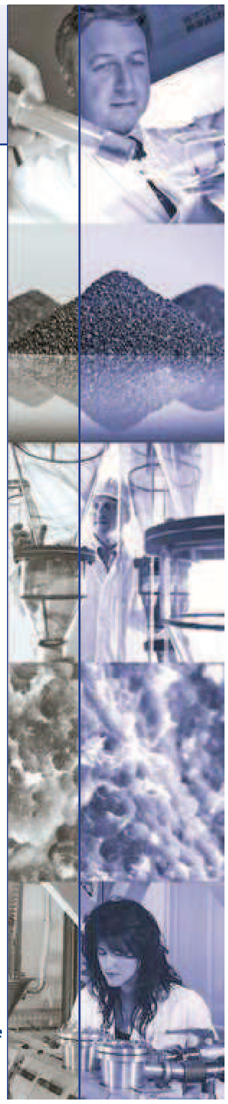
LDOS for the CNT tip functionalized with –COOH group: *disappearing of a resonant state, gap closing;*





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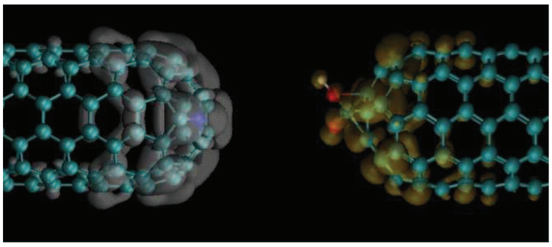
Main conclusion:

While CNT side dopping generaly leads to a decrease in **intra**tube conductivity, contact region functionalisation can improve **inter**tube conductivity due to changes in LDOS;



The results of atomistic-level LDOS calculation can be introduced in mesoscale model in a simple way.

Missing in this picture (future work): e-phonon scattering;

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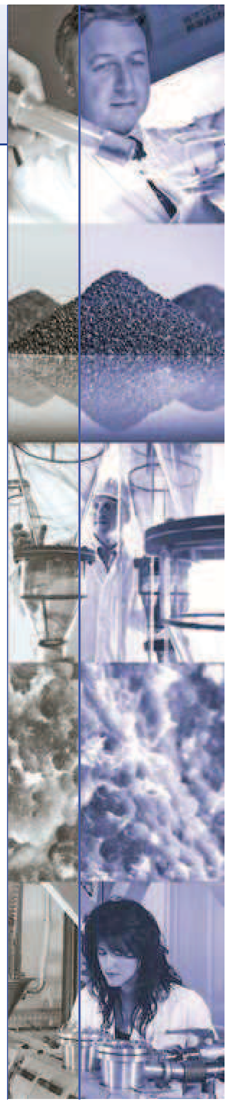

Acknowledgements:

1. The work is a part of the CONTACT project for the tailored supply-chain development of CNT-filled composites with improved mechanical and electrical properties funded by Marie Curie Initial Training Network "CONTACT" (FP7-PEOPLE-ITN-2008-238363) http://www.contactproject.eu/;
2. The Center of Physics of University of Minho research is sponsored by FEDER funds through the program COMPETE- Programa Operacional Factores de Competitividade and by national funds through FCT-Fundação para a Ciência e a Tecnologia, under the project PEst-C-FIS/UI607/2011-2012.

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THANK YOU!

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